

DERWENT-ACC-NO: 1983-847823  
DERWENT-WEEK: 198351  
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TITLE: Recovery of ruthenium oxide coating from electrical device - by redn.  
to ruthenium, and treatment with alkaline soln. contg. chlorine or sodium  
chlorate

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PRIORITY-DATA: 1982JP-0075653 (May 6, 1982)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 58194745 A	November 12, 1983	N/A	003	N/A
JP 91021490 B	March 22, 1991	N/A	000	N/A

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP91021490B	N/A	1982JP-0075653	May 6, 1982

INT-CL\_(IPC): C01G055/00; C22B011/00 ; C22B061/00

ABSTRACTED-PUB-NO: JP58194745A

BASIC-ABSTRACT: Treatment is described of a corrosion-protected electric device  
coated with ruthenium oxide or a mixed crystal containing ruthenium oxide to  
recover the oxide.

The methd comprises reducing ruthenium oxide or a mixed crystal containing  
ruthenium oxide deposited on the electric device to obtain metallic ruthenium,  
treating the metallic ruthenium with an alkali solution contains Cl<sub>2</sub> or sodium  
chlorate to convert the metallic ruthenium to alkaline metal ruthenate M<sup>+</sup> =  
monovalent alkali metal; M<sub>2</sub><sup>+</sup>= and dissolving out the ruthenate in the alkaline  
soln. to remove it from the device and recover ruthenium oxide as ruthenate.

In an example, ruthenium oxide deposited on an alumina body was reduced with H<sub>2</sub>  
at 600 deg.C. to obtain metallic ruthenium. The reduced metallic ruthenium  
was immersed in a KOH soln. containing potassium chlorate, and dissolved out as  
potassium ruthenate in the soln.

CHOSEN-DRAWING: Dwg.0/1

TITLE-TERMS:

RECOVER RUTHENIUM OXIDE COATING ELECTRIC DEVICE REDUCE RUTHENIUM  
TREAT ALKALINE

SOLUTION CONTAIN CHLORINE SODIUM CHLORATE

DERWENT-CLASS: M25

CPI-CODES: M25-E; M25-G28;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1983-124323

**PTO: 2002-2210**

**Japanese Published Unexamined (Kokai) Patent Application No. S58-194745, published November 12, 1983; Application No. S57-75653, filed May 6, 1982; Int. Cl.<sup>3</sup>: C01G 55/00 C22B 61/00; Inventor: Kazunori Tsurumi; Assignee: Tanaka Kikinzoku Kogyo Corporation; Japanese Title: Ruteniumu no Kaishuu Houhou (Method for Recovery of Ruthenium)**

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## **1. Title of Invention**

**Method for Recovery of Ruthenium**

## **2. Claim**

**A method for recovery of ruthenium from an anti-corrosive substrate with ruthenium oxide or mixture crystal substantially made of ruthenium oxide applied, characterized in that, after metal ruthenium has been formed by reducing the ruthenium oxide or the mixture crystal substantially made of ruthenium oxide, the metal ruthenium is separated from the anti-corrosive substrate in the form of ruthenic alkali ( $M^+ RuO_4$  or  $M^{2+} RuO_4$ ) in an alkaline solution that contains a hydrochloric gas or an oxidizing chloride compound ( $M^+$  refers to a monovalent alkali metal;  $M^{2+}$  to a bivalent alkali metal) by a fusing means.**

## **3. Detailed Description of the Invention**

**This invention pertains to methods for recovering ruthenium from anti-corrosive substrates with ruthenium oxide or mixture crystal substantially made of ruthenium oxide applied.**

**Ruthenium oxide is widely used for electric and electronic components as electrical contact point materials and resistor pastes. Ruthenium oxide is also widely used as caustic soda**

electrolyte, sea water electrolyte for cooling water for power plants and electrolytic electrodes for producing alkaline drinking water. In many cases, ruthenium is covered with anti-corrosive ceramics such as alumina and silica and anti-corrosive metals such as titanium, tantalum, zirconium and niobium. As for a conventional recovery method for such ruthenium oxide from the anti-corrosive substrate, ruthenium oxide is physically exfoliated from the substrate first by spraying alumina particles as needed. This exfoliation substance is treated in a peroxide containing fused alkaline salt so as to obtain soluble ruthenic alkali. After this process, the soluble ruthenic alkali is extracted by water or acid. Ruthenium(VIII) oxide is then produced and volatilized in an oxidizing atmosphere so as to recover ruthenium.

However, with prior art recovery method, while ruthenium oxide is mixed with abraded alumina particles during the exfoliating operation, an exfoliation substance at a low ruthenium containing ratio is obtained. When the substrate structure is complicated, even unnecessary sections of the substrate need to be abraded. Even though the amount of ruthenium presented is small, the entire exfoliation substance has to be in the form of a fused salt. Furthermore, an excess amount of an alkaline salt has to be supplied because the alumina particles react with fused alkali. For these reasons, ruthenium is not easily extracted. A large amount of aluminum ions are contained in the residue solution after the extraction of ruthenium. These ions are also necessary to be treated, which involves a higher cost.

The present invention is produced in consideration of the disadvantages as described above and offers a simple method for recovering ruthenium that can achieve a high recovery rate.

The present invention is a method for recovery of ruthenium from an anti-corrosive

substrate with ruthenium oxide or mixture crystal substantially made of ruthenium oxide applied, characterized in that, after metal ruthenium has been formed by reducing the ruthenium oxide or the mixture crystal substantially made of ruthenium oxide, the metal ruthenium is separated from the anti-corrosive substrate in the form of ruthenic alkali ( $M^{+2} RuO_4$  or  $M^{2+} RuO_4$ ) in an alkaline solution that contains a hydrochloric gas or an oxidizing chloride compound by a dissolving means ( $M^{+}$  refers to a monovalent alkali metal;  $M^{2+}$  to a bivalent alkali metal). More specifically, the present invention primarily provides a separation process of metal ruthenium from the substrate by a fusion means, which is transformed from ruthenium oxide. In the invention, the reason that metal ruthenium is formed by reducing ruthenium oxide or mixture crystal substantially made of ruthenium oxide at the first step is that ruthenium oxide is not easily fused. As for the reducing methods, the following types can be used: a regular hydrogen reduction; a reverse electrolytic reduction; a thermit reduction. After the formation of metal ruthenium, it is immersed in an alkaline solution that contains a chlorine gas or an oxidizing chlorine compound. In this case, the alkaline solution that contains the chlorine gas or the oxidizing chlorine compound is used because metal ruthenium does not dissolve in an alkaline solution that contains the chlorine compound alone. As for the oxidizing chlorine compound, the following substances are used: chlorate; perchlorate; chlorine oxide; hypochlorous acid. Chlorate includes ammonium chlorate and potassium chlorate. Perchlorate includes magnesium perchlorate and calcium perchlorate. These components can be selected according to the materials for the anti-corrosive substrate as needed. If the fusing speed is low when the mixture crystal made of ruthenium oxide is reduced, the mixture crystal can be fused by an electrolytic or heating means. When metal

ruthenium is fused with these baths, metal ruthenium alone can be separated in the form of ruthenic alkali by a fusing means. If monovalent alkaline metal is used as the alkaline solution, metal ruthenium is fused in the form of  $M^{+2} RuO_4$ . If bivalent alkali metal is used, metal ruthenium is fused in the form of  $M^{2+} RuO_4$ . Because neither form of ruthenic alkali contains other interfering metal elements in the solution, metal ruthenium is recovered by easily producing and volatilizing it. The embodiments are described hereinbelow.

**[Embodiment 1]**

60 10 x 10 x 1 mm ruthenium oxide coating titanium substrate are reduced in a hydrogen atmosphere at 500°C for 20 minutes so as to reduce a minute amount of ruthenium oxide to metal ruthenium. 10 pieces of the substrates are reacted to a 30% caustic soda solution of 80 ml and a hypochlorous soda with 12% effective chlorine at a room temperature for 2 hours while the mixture is agitated. By repeatedly applying these steps, the remaining 50 substrates are treated. When the surfaces of the substrate are analyzed by an X ray microanalyzer after rinsing the substrates with water, ruthenium is not detected. Next, while a ruthenic alkali containing solution is heated to 80°C, a chlorine gas is blown. Due to the use of the chlorine gas, ruthenium is oxidized and volatilized. After the oxidized and volatilized ruthenium has been absorbed in a chloric acid solution so as to obtain ruthenium chloride. When this solution is concentrated and solidified, brown ruthenium chloride crystal of 1.4 g is obtained.

**[Embodiment 2]**

By reducing 100 3 x 3 x 1 mm alumina substrates wherein ruthenium oxide is baked with glass in a hydrogen atmosphere at 600°C for 60 minutes, ruthenium oxide is transformed into metal ruthenium. These substrates are reacted in a 30% potassium hydroxide solution of 100 ml and a 10% potassium chlorate solution of 30 ml for 24 hours while the mixture solution is agitated. When the surfaces of the substrate are analyzed by an X ray microanalyzer after rinsing the substrates with water, ruthenium is not detected. Next, while a ruthenic alkali containing solution is heated to 80°C, a chlorine gas is blown. Due to the use of the chlorine gas, ruthenium is oxidized and volatilized. After the oxidized and volatilized ruthenium has been absorbed in a chloric acid solution so as to obtain ruthenium chloride acid. When this solution is concentrated and solidified, brown ruthenium chloride crystal of 2.5 g is obtained.

**[Embodiment 3]**

After 100 rivet electric copper contact points of a 2 φmm head diameter wherein ruthenium oxide at about 2 μm is coated on the surfaces thereof have been reduced in a hydrogen atmosphere at 500°C for 10 minutes, they are immersed into a caustic soda solution of 80 ml. The caustic solution is then heated to 80°C. Following this, ruthenium oxide reduced in advance after blowing a chlorine gas is oxidized and volatilized. Th oxidized and volatilized ruthenium oxide is then absorbed in a hydrochloric acid solution so as to form ruthenium chloride acid. When this solution is condensed and solidified, brown ruthenium chloride crystal of 0.5 g is obtained. Ruthenium is not identified in the copper contact point material.

As described above, according to the ruthenium recovery method for the present invention, ruthenium is recovered without melting the substrate, by reducing ruthenium oxide

**on the substrate surface to metal ruthenium. Because of this, the steps are simplified, and a cost-saving is achieved. A high quality product is also achieved.**

**Translations Branch  
U.S. Patent and Trademark Office  
4/1/02  
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